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# A study of stearyl alcohol bloom on Dan Hill PVC dolls and the influence of temperature

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A study was conducted to investigate white bloom found on more than 130 polyvinyl chloride (PVC) dolls from the 1980s and 1990s produced by the Danish factory Dan Hill Plast A/S. The bloom was discovered on the dolls after 10 years of storage in a climate controlled facility with average temperature at 11–12°C and a relative humidity at 50 ± 5%. Analysis of the dolls and the bloom was carried out using Fourier transform infrared spectroscopy, which revealed that the bloom consisted primarily of stearyl alcohol. Subsequent analysis with gas chromatography–mass spectrometry showed a minor presence of cetyl alcohol. It is proposed that the alcohol had been added as a lubricant to aid flow during processing. The stearyl alcohol was almost completely reabsorbed into the PVC dolls following one month storage at room temperature, suggesting that low temperature storage played a decisive role in the appearance of the bloom. It is likely that a decrease in temperature has led to a decrease in compatibility of the stearyl alcohol in the PVC compound, thus promoting its exudation. This paper also discusses an extreme bloom of white crystals on other PVC dolls of unknown provenance.

**Keywords:** PVC dolls, Migration, Lubricant, Stearic acid, Stearyl alcohol, FTIR, GC–MS

## Introduction

In 2014 when the local Cultural History Museum in Glud, Denmark audited its collections, it was observed that a large number of plasticized polyvinyl chloride (PVC) dolls (DanDolls), made by the factory Dan Hill Plast A/S, were partially covered with a white waxy material on their plastic parts. The phenomenon had not been observed on the dolls before storage. The white exudates, which were easily smeared by touching, appeared to have migrated from inside the dolls. No difference in the level of bloom was observed between areas which were covered by clothes or paper, and areas which were left uncovered. Moreover, neither the paper nor the clothes stuck to the plastic surface, indicating that the appearance of the bloom was not a result of extraction caused by the packing materials or clothes. No sign of PVC degradation in the form of colour change was observed on any of the dolls. The bloom was very distracting in particular on the dark-coloured dolls (Fig. 1A and B).

The bloom was confirmed on more than 130 dolls dating from the early 1980s onwards. However, since Glud Museum has more dolls from Dan Hill Plast not yet assessed, the number of affected dolls is believed to be much higher. The dolls had been handed over to the museum in the year 2000 together with squeaky toys and money boxes shortly after Dan Hill Plast had closed down its production of these items. The dolls were on display for two years, before they were wrapped in acid free tissue paper and stored in boxes in the Shared Storage Facility in Vejle. This facility is built on the concept of passive climate control with well isolated concrete walls and nonisolated floors which restrict large fluctuations of the temperature and relative humidity (RH) during the year (Knudsen & Rasmussen, 2005). The climatic data from the storage records show a yearly average temperature of 11–12°C and a RH of 50 ± 5%. In the summer, the temperature rarely reached above 16°C and in the winter rarely below 7°C with RH remaining within the range stated above.

The appearance of bloom after removing the dolls from approximately 10 years of uninterrupted storage raised important questions: was the relative cold storage temperature the cause of the bloom? Is

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**Figure 1** Dolls showing white bloom. The bloom from DanDolls (A and B) is particularly discernable on the dark-coloured doll (A). Plastic dolls of unknown provenance donated to the Conservation Centre in Vejle (C and D). The crystalline bloom in (C and D) is loosely bound and falls away easily when touched.

the phenomenon restricted to dolls produced by Dan Hill Plast or is it expected to be found on PVC dolls in general? Is the bloom safe to clean off, or is it potentially harmful to handle? How should the dolls be stored in the future to prevent this? These conservation questions promoted this study into the fabrication and material composition of DanDolls and the effects of long-term storage.

A plasticized PVC doll (troll) and a plasticized PVC doll head of unknown date and unknown provenance donated to the Conservation Centre in Vejle because of their spectacular bloom of white, loosely bound crystals (Fig. 1C and D) were also examined in this study. The crystalline character of the bloom is very different from the waxy bloom of the DanDolls, and the crystals fall off when touched. In contrast to the DanDolls, the storage of these dolls before they were donated to the Conservation Centre in Vejle is not known.

Fourier transform infrared (FTIR) spectroscopy was the main method used for the investigation of the dolls since it is a relatively simple and fast method capable of identifying a wide range of plastic types and additives. Additionally, gas chromatography–mass spectrometry (GC–MS) was used to further characterize plasticizer and some minor components in exuded material from two DanDolls.

The investigation into the different blooming phenomena presented in this study is of interest to other museums dealing with long-term storage of PVC objects in their collections.

### The history of DanDolls

The founders of Dansk Vacuum Plast A/S Else and Ejnar Madsen began the production of plastic items in 1957 in a former laundry in the village Brabrand near Aarhus. Ejnar Madsen, a skilled mechanic, started the production of squeaky toys inspired by the production methods used in chocolate moulding. By means of two shells of aluminium moulds held together by clips, the fluid plastic mass was dispersed by rotation while heated. By this technique, Ejnar Madsen succeeded in fabricating hollow materials in plastic. After a few years, the factory bought new machinery from England intended for this specific kind of rotational moulding. In England, this manufacturing process was more common at the time than it was in Denmark (Madsen, 2015).

Quickly the location in Brabrand became too small and in 1958 the company moved to an old power station in the village of Hornsyld in the south-east of Jutland. After a couple of years, the company expanded the production to include plastic dolls, play balls, and money boxes (Dan Hill Plast A/S; Luckey, 1992). In the late 1980s, the company changed its name to Dan Hill Plast A/S, but already during the 1970s the dolls were sold under the name of DanDoll. The company specialized in rotational moulding and over time made hollow articles for an increasing variety of purposes (Dan Hill Plast A/S; Madsen, 2015).

In 1981, the company started the production of a doll series called ‘Children of our World’ following an enquiry from an American merchant. At first they were sold to kindergartens in the U.S. only, but later on they were also distributed in Australia, Japan, South Korea, Canada, and continental Europe. Over the years, Dan Hill Plast played a prominent role in the manufacturing of high quality plastic dolls in Denmark in particular for use in kindergartens. In 1990, the company introduced a new creation of large dolls (65 cm) especially made for doll collectors all over the world. This creation was called ‘The United Children of our World’ representing children from different continents wearing their national dresses. At this time, the yearly output of dolls was about 80 000 (Luckey, 1992; Madsen, 2015).

In the late 1990s, the production of dolls in Denmark became too expensive in comparison to dolls made abroad, and the company chose to focus on other objects made of plastic such as fenders, buoys, and playground toys. Today Dan Hill Plast is

a company with 55 employees still located in the village of Hornsyld.

### Manufacturing of DanDolls

The production of flexible PVC objects can be divided into two main processes: the compounding (mixing) of the PVC with additives and the fabrication process, e.g. shaping or moulding into the final product. Additives are essential to make PVC processable and to ensure end-use properties. The most abundant additive in flexible PVC is in general the plasticizer, and a content of 10–40% is common in PVC toys (Stringer *et al.*, 2000; Babich *et al.*, 2004).

Plasticizers confer flexibility to the final product and improve workability during processing. The most common plasticizers are the phthalates due to their good compatibility and performance with PVC and low cost (Krauskopf, 2003). Of these, diisononyl phthalate (DINP), has in recent times been the most frequently used plasticizer in children toys and articles (Stringer *et al.*, 2000; Babich *et al.*, 2004), until new regulations introduced in the late 1990s restricted the use of phthalates in these items due to health concerns (European Parliament Council, 1999, 2005). Other additives in flexible PVC are generally added in relatively small amounts and include stabilizers, which confer stability to the PVC polymer, and lubricants, which aid processing of the compound. Moreover, colourants and fillers can be added as well as other additives, depending on the performance requirements of the end product (Wilkes *et al.*, 2005).

The PVC compound used for rotational moulding is traditionally a plastisol, which is a suspension of PVC particles in plasticizer. The fluid plastisol is poured into the moulds, which are then rotated about their vertical and horizontal axes, allowing the plastisol to be uniformly distributed (Wilkes *et al.*, 2005). Heating of the plastisol causes resin particles to absorb plasticizer and fuse into a homogeneous and solid mass which exhibits minimal shrinkage on cooling (Chanda & Roy, 2007). The final products are hollow parts with uniform wall thickness ideal for doll production.

Compounding of PVC with its additives is often carried out by specialist companies (Elias, 1992). However, Dan Hill Plast not only fabricated the dolls, but the factory also compounded their own PVC. This was done with a conventional dough mixer provided from a bread factory. The compound had to be kept under constant stirring until shortly before use to prevent precipitation (Mortensen, 2015).

The rotation machines were equipped with several interchangeable copper moulds of doll heads, limbs, and torsos, allowing cast products of different shapes to be made at the same time. After casting the doll, parts were assembled and the head was decorated.

The hair was made of nylon if not part of the cast head. Eyes, eyebrows, and lips were spray painted using templates for each colour, a process which involved several steps. In areas which could not be reached by spray paint the colours were applied by brush. For the more elaborate dolls, the eyes and eyelashes were not painted but inserted. In the last steps, the dolls were dressed and packed. The sewing of the clothes involved several seamstresses who worked from home (Mortensen, 2015).

The designer of the dolls and of many other toys produced by Dan Hill Plast was John Nissen, a manikin designer from Copenhagen. One of his doll series, ‘the Fashionable’, created in 1987, even represented miniature manikins dressed in the fashion of the twentieth century (Fig. 2A and B). Else Madsen, co-founder of Dan Hill Plast, designed the clothes for this series and other, prestigious dolls. In particular, the dresses for the doll series ‘The United Children of our World’ (Fig. 2C and D) created in 1990–91 required much effort and research. Pearls and textiles were sometimes imported directly from the respective countries they represented. One of the most peculiar examples was the girl from the Philippine Islands (Fig. 2C) whose butterfly sleeves were woven out of pineapple fibre (Luckey, 1992).

### Problems of additive release from PVC objects

The potential release of additives from PVC is a drawback of probably the most outstanding of its qualities — the ability to accept a wide range of substances, making it possible to modify it into a variety of end products (Cadogan & Howick, 1992). Some additives tend to migrate and bloom from the surface with time, as is the case with DanDolls and the other dolls shown in Fig. 1.

The release of plasticizers is probably the best-documented and in general the most problematic of additive losses. A considerable loss of plasticizer leads to degradation in the form of stiffness and shrinkage, and exuded plasticizers may result in sticky surfaces, which attract dirt and pollutants. One way to decrease the loss of plasticizer is to reduce volatilization from the surface. Volatile loss takes place continually and is controlled by factors such as the vapour pressure of the additive and diffusion of the additive to the surface. In general, the vapour pressure is the controlling factor for volatile loss, though diffusion rate might take over, for example in well ventilated conditions (Wilson, 1995). Vapour pressure increases with temperature, and thus the reduction of volatilization can be obtained by lowering the temperature (Wilson, 1995). Shashoua has shown that decreasing the temperature from ambient to  $-20^{\circ}\text{C}$  reduced the migration of plasticizer by a factor of 15 (Shashoua, 2004). Contraction and stiffening on cooling are factors that





**Figure 2** Examples on DanDolls produced by Dan Hill Plast A/S. Dolls from the series 'The Fashionables' (A and B) representing (A) the 1960s: Hot Pants and Long Legs and (B), the 1970s: Jeans and Dreams (height: 40 cm). Dolls from the series 'The United Children of our World' (C and D). Philippini, the girl from the Philippines (C) and Ivalo, the girl from Greenland (D) (height: 65 cm).

should be taken into consideration; however, for non-degraded PVC these physical changes are reversible upon return to ambient temperatures (Shashoua, 2004).

Less known than plasticizer loss is the loss of lubricants from PVC compounds, though, since lubricants are in general the least compatible constituent, they are the most liable to exudation (Wilkes *et al.*, 2005). Lubricants function as processing aids and they may act by improving melt flow of the PVC compound during heating, lowering the melt viscosity, or improving release from the metal surface of processing equipment such as the rotational moulds in doll production (Nass & Heiberger, 1988).

The proportion of lubricants added to plasticized PVC is rather small, about 0.25–1%. The most commonly used is stearic acid (octadecanoic acid) due to its excellent slipping properties (Sears & Darby, 1982). Stearic acid has a great affinity for metal oxides which form on metal surfaces, e.g. of the moulding equipment, and during processing sweats out to form a film between the PVC compound and the metal, thus acting as a slipping agent (Wilkes *et al.*, 2005; Shashoua, 2008). Stearic acid is poorly compatible with PVC, and if any remains in the compound after processing, there is a high risk of exudation from the surface with time. Indeed, stearic acid has been reported to bloom on a PVC doll from the 1960s after 20 years of storage, forming a white brittle layer on the surface (Shashoua, 2008).

## Experimental

### Sampling

Samples from 17 DanDolls were taken on the same day as the dolls were taken out of cold storage. An

overview of the dolls and the localization of sampling are given in Table 1. The exact date of manufacture of the dolls is not known. Probably, all examined dolls were made in the 1980s or 1990s, the ones with the lowest museum number being from the beginning of this period. Moreover, plastic samples were taken from the backside border of the neck from the two dolls of unknown provenance. Samples of bloom from all dolls were carefully scraped off with a scalpel under the microscope.

### ATR-FTIR spectroscopy

Attenuated total reflection (ATR)-FTIR spectra were recorded on a Perkin Elmer Spectrum One FTIR spectrometer, fitted with a Universal ATR sampling accessory including a one bounce composite zinc selenide and diamond crystal. Spectra of the samples were recorded over the range of 4000–650  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$  and 4 accumulations.

### GC-MS

GC-MS analyses were performed with an Agilent 6890/5973N system. Samples of scrapings were dissolved in methyl *tert*-butyl ether (MTBE) for analysis. Samples of plastic were placed in MTBE overnight; the plastic samples were then removed and the solution analysed. All samples were analysed both in splitless and in split mode (split ratio 10:1) to account for different concentrations of components. A solvent blank was run between each measurement.

The GC column was a fused silica capillary column, HP-5MS (30 m, 0.25 mm i.d., 0.25  $\mu\text{m}$  film thickness). Helium was used as the carrier gas at a flow rate of 1.3  $\text{mL min}^{-1}$ . The temperature programme used an initial temperature of 60°C, held for 5 minutes and

**Table 1** Description of dolls sampled and summary of FTIR results

Type of doll	Museum number	Sample localization	FTIR of bulk plastic	FTIR of bloom
DanDoll	773 × 376	Left leg	PVC and <i>ortho</i> -phthalate	Fatty alcohol
DanDoll	773 × 383	Right leg	PVC and <i>ortho</i> -phthalate	Fatty alcohol
DanDoll	773 × 398	Head	PVC and <i>ortho</i> -phthalate	Fatty alcohol
DanDoll	773 × 408	Left leg	PVC and <i>ortho</i> -phthalate*	Fatty alcohol <sup>†</sup>
DanDoll	773 × 420	Head	PVC and <i>ortho</i> -phthalate	Fatty alcohol
DanDoll	773 × 437	Head	PVC and <i>ortho</i> -phthalate	Fatty alcohol
		Right foot	PVC and <i>ortho</i> -phthalate	Fatty alcohol
DanDoll	773 × 466	Corpus	PVC and <i>ortho</i> -phthalate	Fatty alcohol
DanDoll	773 × 478	Right arm	PVC and <i>ortho</i> -phthalate	Fatty alcohol
DanDoll	773 × 493	Right foot	PVC and <i>ortho</i> -phthalate	Stearyl alcohol <sup>‡</sup>
DanDoll	773 × 496	Head	PVC and <i>ortho</i> -phthalate	Fatty alcohol
DanDoll	773 × 501	Head	PVC and <i>ortho</i> -phthalate	Fatty alcohol
DanDoll	773 × 503	Right leg	PVC and <i>ortho</i> -phthalate	Fatty alcohol
DanDoll	773 × 516	Corpus	PVC and <i>ortho</i> -phthalate	Fatty alcohol
		Head	PVC and <i>ortho</i> -phthalate	Fatty alcohol
		Left leg	PVC and <i>ortho</i> -phthalate	Fatty alcohol
		Right arm	PVC and <i>ortho</i> -phthalate	Fatty alcohol
DanDoll	773 × 523	Head	PVC and ATBC	Fatty alcohol
		Right leg	PVC and <i>ortho</i> -phthalate	Fatty alcohol
		Left leg	PVC and <i>ortho</i> -phthalate	Fatty alcohol
DanDoll	773 × 525	Head	PVC and <i>ortho</i> -phthalate	Fatty alcohol
		Left leg	PVC and <i>ortho</i> -phthalate	Fatty alcohol
DanDoll	773 × 529	Head	PVC and <i>ortho</i> -phthalate	Fatty alcohol
		Right leg	PVC and ATBC <sup>§</sup>	Fatty alcohol <sup>†</sup>
		Left leg	PVC and ATBC	Fatty alcohol
		Arm	PVC and ATBC	Fatty alcohol
DanDoll	773 × 545	Head	PVC and ATBC	Fatty alcohol
Doll (troll)	No number	Head	PVC and <i>ortho</i> -phthalate	Stearic acid
Doll (head)	No number	Head	PVC and <i>ortho</i> -phthalate	Stearic acid

\*GC–MS result: DINP.

<sup>†</sup>GC–MS result: stearyl alcohol and minor presence of cetyl alcohol.<sup>‡</sup>Sample cleaned with acetonitrile.<sup>§</sup>ATBC confirmed by GC–MS.

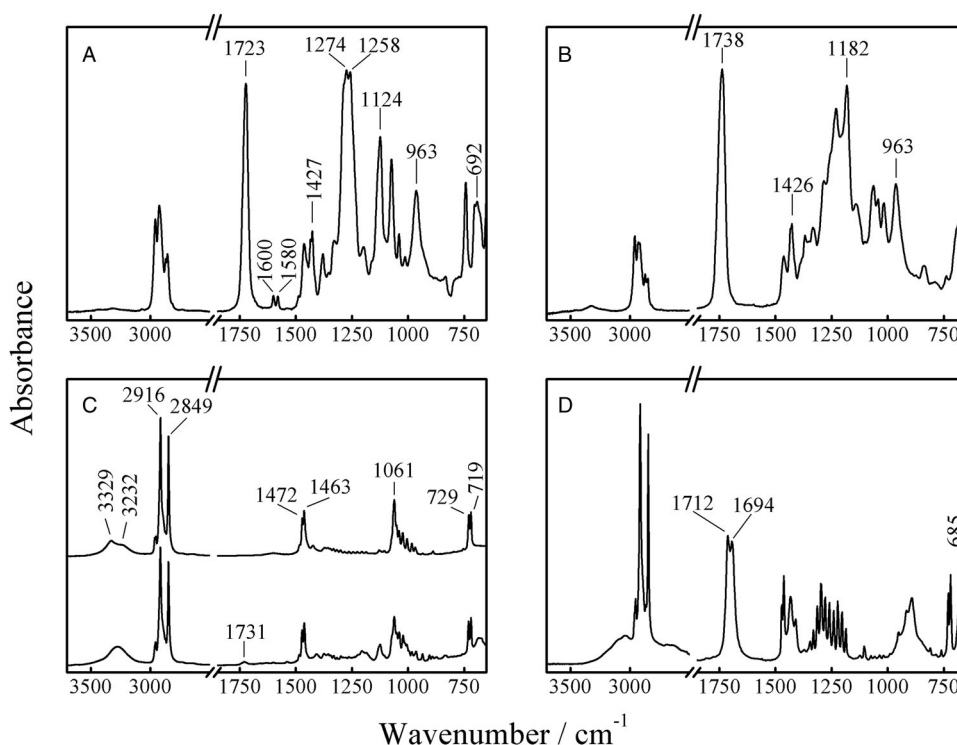
ramped at 20°C min<sup>−1</sup> to 300°C and held for 8 minutes; total run time was 25 minutes. The inlet temperature was 300°C and the MS transfer line 280°C. The mass spectrometer used Electron Impact (EI+) ionization (70 eV), operating in scan mode from *m/z* 30 to 700 every 0.5 second. The ion source temperature was 230°C.

## Results and discussion

An overview of the FTIR results is given in Table 1. FTIR spectra of plastic samples from 15 DanDolls were similar; a representative spectrum is shown in Fig. 3A from DanDoll 773 × 493. The result suggests PVC plasticized with an *ortho*-phthalate. Such spectra are usually dominated by the plasticizer identified by stretching vibrations of C–H in the region 3000–2800 cm<sup>−1</sup>, C=O stretching at 1723 cm<sup>−1</sup>, C–O stretching at 1274 and 1124 cm<sup>−1</sup>, and bands corresponding to C–C stretching of the aromatic ring at

1600 and 1580 cm<sup>−1</sup> (Burke *et al.*, 1985; Beltrán & Marcilla, 1997; Ploeger *et al.*, 2008). Characteristic bands for PVC are the CH<sub>2</sub> deformation at 1427 cm<sup>−1</sup>, CH deformation at 1258 cm<sup>−1</sup>, C–C stretching at 963 cm<sup>−1</sup>, and C–Cl stretching at 692 cm<sup>−1</sup> (Socrates, 2001; Shashoua, 2008; Mitchell *et al.*, 2013). By FTIR it is not possible to determine what kind of *ortho*-phthalate is present.

Plastic samples from three DanDolls gave spectra different from the others and, apart from bands corresponding to PVC, consistent with a reference of acetyl tributyl citrate (ATBC). A representative spectrum from doll 773 × 523 is shown in Fig. 3B. The C=O absorption at 1738 cm<sup>−1</sup> is observed at somewhat higher wavenumbers than the phthalate, and in particular the strong asymmetric C–O stretching at 1182 cm<sup>−1</sup> is typical of citrates (Socrates, 2001). ATBC is the most commercially important of the citrate plasticizers (Wilson, 1995). Traditionally, they



**Figure 3** FTIR spectra of bulk plastic and bloom. (A) Plastic of DanDoll 773 × 493 plasticized with phthalate; (B) plastic of DanDoll 773 × 523 plasticized with ATBC; (C) crude scraping of stearyl alcohol bloom from DanDoll 773 × 493 (bottom) and of the cleaned sample (top); (D) stearic acid bloom from doll head.

have only found minor use due to their high cost, which is about three times the price of phthalates. They started to gain interest as an alternative in children's toys at the end of the 1990s, as the phthalates were phased out (Marcilla *et al.*, 2004; Gil *et al.*, 2006). The findings indicate that these dolls are from the latest production from Dan Hill Plast, probably produced shortly before Dan Hill Plast closed down its doll production around 2000. This also conforms to the high museum numbers (Table 1). Noteworthy is that ATBC and phthalates are used in different body parts of same dolls, suggesting that the body parts are from different batches.

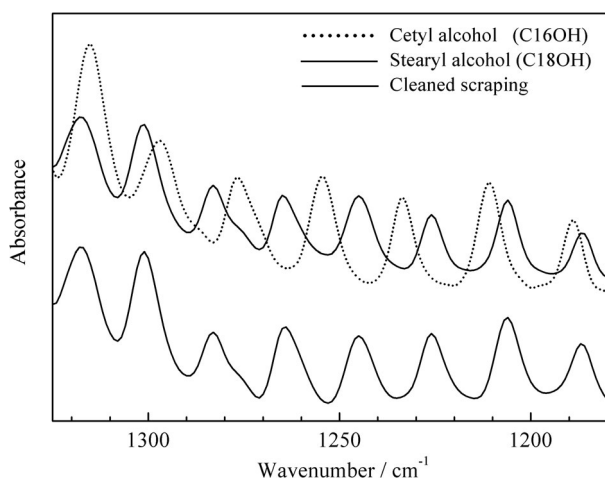
Spectra for the white bloom from all DanDolls were similar to the example shown in Fig. 3C (bottom) taken from DanDoll 773 × 493. Vibration bands corresponding to long aliphatic chains at 2916 and 2849  $\text{cm}^{-1}$  (C–H stretching), 1472, 1463  $\text{cm}^{-1}$  (C–H deformation), 729 and 719  $\text{cm}^{-1}$  (C–H rocking) in combination with broad O–H stretching around 3270  $\text{cm}^{-1}$  show the presence of a long-chain fatty alcohol. The strong C–O stretching in the region 1090–1000  $\text{cm}^{-1}$  is typical of primary alcohols (Socrates, 2001). A low intensity band at 1727–1733  $\text{cm}^{-1}$  was observed in the spectra of the bloom from the phthalate-containing dolls and at 1741–1744  $\text{cm}^{-1}$  in the spectra of the bloom for those containing ATBC. The small band is possibly due to a carbonyl group. However, the frequency is different from that of the C=O groups in the plasticizer detected in

the plastic samples, and GC–MS analysis only shows a minute amount of plasticizer in the scraping. Hence, an unambiguous assignment of these peaks is not possible.

Identification of the aliphatic alcohol was hampered due to obscuration of the fingerprint region. To obtain a clean spectrum, the white scraping was cleaned with acetonitrile; this solvent was used as the fatty alcohols are less soluble in acetonitrile compared to other organic solvents. A sample of scraping was placed in a 5 mL test tube and 2 mL acetonitrile added. The mixture was shaken for a few minutes then centrifuged, and the acetonitrile solution removed. The residue was air-dried overnight, and an FTIR spectrum of the dried residue was recorded.

By washing the sample with acetonitrile, a clean spectrum of stearyl alcohol (octadecan-1-ol) was obtained (Fig. 3C, top). In particular, bands in the region 1310–1185  $\text{cm}^{-1}$ , related to  $\text{CH}_2$  wagging modes (Robinet & Corbeil, 2003), were now visible. Indeed, comparing reference spectra of different aliphatic alcohols showed that the number of bands in this region increase with the number of C atoms, which makes it possible to distinguish various fatty alcohols from one another. This observation has also been noted for fatty acids (Robinet & Corbeil, 2003). In Fig. 4, the spectrum of the cleaned sample in the region 1325–1180  $\text{cm}^{-1}$  is shown together with reference spectra of stearyl and cetyl alcohol (hexadecan-1-ol). The spectrum is in accordance with stearyl





**Figure 4** Detail of FTIR spectrum of the bloom from DanDoll 773×493 cleaned with acetonitrile (bottom) compared with reference spectra of cetyl and stearyl alcohol (top) in the 1325–1180 cm<sup>-1</sup> region.

alcohol having eight bands in this region whereas cetyl alcohol has seven, and the bands between the two alcohols are out-of-phase.

Further analysis of the white scraping and of the bulk plastic was carried out using GC–MS. The total ion chromatogram (TIC) and the corresponding mass spectra are shown in Figs. 5 and 6. The TICs given are from the splitless measurements in order to enhance the visibility of minor compounds.

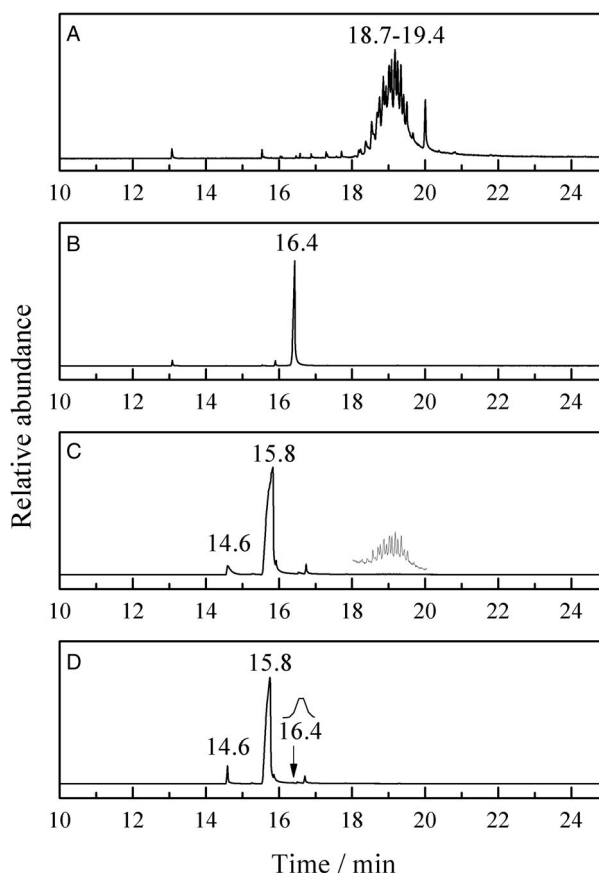
The chromatograms of the extracts from plastic samples identified by FTIR to contain phthalate (773×493) and ATBC (773×529) plasticizer are seen in Fig. 5A and B, respectively. Fig. 5A shows the presence of the plasticizer eluting from 18.7 to 19.4 minutes. The typical cluster of peaks centred at c. 19 minutes is in accordance with a mixture of isomers and the averaged mass spectrum (Fig. 6A) shows characteristic ions at  $m/z$  149 and 293. This is in agreement with an analysed reference sample of DINP and literature data (Earls *et al.*, 2003). The single peak at 16.4 minutes in Fig. 5B is in agreement with a reference sample of ATBC, and the mass spectrum in Fig. 6B shows characteristic ions for ATBC including  $m/z$  185 and 259 (Gimeno *et al.*, 2014). Apart from the peak at 20.0 minutes in Fig. 5A, which based on its mass spectrum could be identified as the antioxidant and UV stabilizer 4,4'-diocetylphenyl amine, no other peaks seen in the TICs of the plastic extracts were identified.

As mentioned previously, DINP was until recently the most common plasticizer in children's toys and chosen as such because of its resistance to migration compared to other phthalates of lower molecular weight. Since further dolls were not analysed with GC–MS, it is not possible to say, however, whether all phthalates identified with FTIR are of the DINP type.

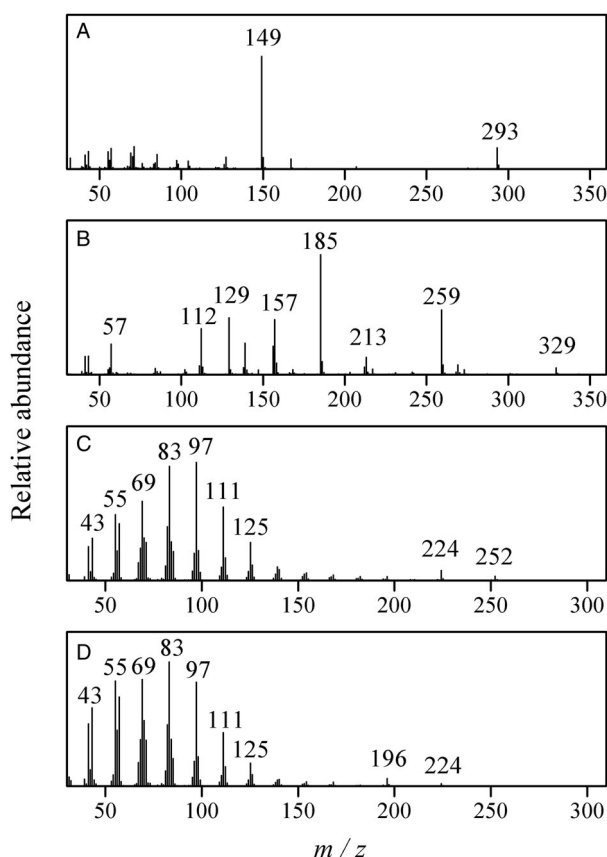
The TICs from samples of the white scraping coming from PVC dolls plasticized with DINP or ATBC are shown in Fig. 5C and D. Both chromatograms are similar and show a major peak eluting at 15.8 minutes for stearyl alcohol, and a smaller peak at 14.6 minutes for cetyl alcohol. The corresponding mass spectra are shown in Fig. 6C and D, respectively. Both mass spectra show the characteristic fragmentation pattern of a long-chain alcohol with the highest visible  $m/z$  value at  $[M-18]^+$  (due to loss of water). Cetyl and stearyl alcohols are the most common fatty alcohols derived from natural sources (Noweck & Grafahrend, 2012). In this case, the former is probably an impurity in the latter.

The enlargements inserted in Fig. 5C and D display the plasticizer peaks. Their low intensity indicates that only a minute amount of plasticizer is present in the scraping. The minor peak at 16.7 minutes, present in both TICs from the scrapings, gave a mass spectrum similar to the other fatty alcohols but could not be readily identified.

Stearyl alcohol is not a common additive in flexible PVC compounds. Nevertheless, fatty alcohols are sometimes used in the polymerization process for



**Figure 5** TIC of plastic samples and of white bloom. (A) Plastic sample 773×408 containing phthalate plasticizer; (B) plastic sample 773×529 containing ATBC plasticizer; (C) white bloom from 773×408; (D) white bloom from 773×529. The minor presence of plasticizer in the bloom is shown as enlarged inserts.



**Figure 6** Mass spectra corresponding to the major peaks in the TICs. (A) DINP; (B) ATBC; (C) stearyl alcohol; (D) cetyl alcohol.

PVC resins used for plastisols. As mentioned previously, plastisol is the most common type of PVC compound used in rotational moulding. Resins used for such compounds require a very fine particle size, which can be made by either the emulsion or micro-suspension process. Both processes take place in a watery phase and involve the use of surfactants. Sodium lauryl sulphate is the most common surfactant used and in the micro-suspension process can be used in combination with long-chain fatty alcohols. In the final PVC resin, residual surfactants may comprise 2–4% of the polymer weight. Due to the surfactant coating, the particles treated by these methods are readily wetted by plasticizers at the compounding stage (Wilkes *et al.*, 2005).

If the stearyl alcohol originates from such a surfactant system, it would have been part of the PVC powder product bought by Dan Hill. However, this is not very likely since, if the use of fatty alcohols in the polymerization process was known to lead to a risk of blooming at a later stage, this would probably be reported in the literature, and this is not known to the authors. The polymerization process is carried out by specialist companies and the risk of failure is relatively low. Anionic surfactants, which would have been used with stearyl alcohol, were not identified in the bloom.

More likely is perhaps that the stearyl alcohol has been added to the PVC compound by Dan Hill Plast themselves. Though not a common additive in flexible compounds, stearyl alcohol is a common lubricant added to rigid PVC where it acts as a flow-promoter during processing. Such lubricants are rarely used in flexible compounds, because the plasticizers also act as flow-promoters (Nass & Heiberger, 1988). It was not possible to get an answer from Dan Hill Plast whether or not they have used flow-promoters in their flexible PVC products.

The spectra of the bulk plastic of the doll head and troll (Fig. 1C and D) were similar to the spectrum of the DanDolls showing PVC plasticized with an *ortho*-phthalate (spectra not shown). The spectrum of the white crystals was in accordance with a reference of stearic acid. The splitting of the C=O stretching band in two at about 1710 and 1690  $\text{cm}^{-1}$  observed in our spectrum (Fig. 3D), has been noted earlier for the B-form of stearic acid (Holland & Nielsen, 1962). As mentioned previously, stearic acid is a common additive for flexible PVC due to its excellent slipping properties, but is prone to exude with time due to incompatibility.

Interesting observations were made on the DanDolls after they were taken out of cold storage and brought to the conservation studio. After about a month, a significant part of the bloom had disappeared (Fig. 7). The dolls were taken out in the summertime to the climate controlled studio where the average temperature and RH were at 24°C and 46%, respectively. The experiment was repeated in the wintertime, with average *T* and RH at 19°C and 45%, respectively. No difference in the reduction of bloom was observed between dolls, which were wrapped and put in boxes (to simulate the storage conditions), and dolls which were left unwrapped. The reduction of bloom appeared to a somewhat lesser extent in the winter than in the summertime.

Since RH in the studio was close to the RH in the storage facility, this is not believed to have any significant influence on the disappearance of the bloom. Moreover, since no difference was observed on wrapped and unwrapped dolls, microclimatic influence is not likely to play any role either. Rather the observations suggested that the increased temperature in the conservation studio had caused the reduction of stearyl alcohol on the surface of the dolls.

In the literature, stearyl alcohol is described as a volatile (Zweifel *et al.*, 2009). However, no measurable changes (visual and weight) were observed in a thin film of stearyl alcohol cast from 96% ethanol and left for two months in a ventilated fume hood. This suggests that the stearyl alcohol did not disappear due to evaporation.

About four months after the dolls were brought back to cold storage, it was observed that the stearyl



**Figure 7** The white bloom of DanDoll 773 × 503 is clearly visible when just taken out of cold storage (A). After a month at room temperature, the bloom has almost disappeared (B). Bloom reemerging on the doll after six months of cold storage (C).

alcohol migrated back to the surface of the dolls, though at a much slower rate than it had disappeared. After six months, this was clearly visible though the bloom was far less pronounced than it had been the first time the dolls were taken out of cold storage (Fig. 7).

The explanation for the appearance of stearyl alcohol on the surface of the dolls is probably found in incompatibility between the stearyl alcohol and the plastic matrix at the low storage temperatures, forcing stearyl alcohol to the surface. As a result of the warmer temperatures in the conservation studio, the stearyl alcohol is reabsorbed as compatibility is enhanced.

Compatibility depends on the saturation concentration or compatibility limit, which is an expression for how much additive the compound can accept at a certain temperature. In general, the limit increases with temperature. This factor is of particular concern at the high processing temperatures, by which the PVC compound is able to accept a relatively high amount of additives. If too much is added, the compound becomes supersaturated when cooled down, which causes precipitation of the additive. This leads to a haze in clear compounds and moreover, the risk of additive exudation (Zweifel *et al.*, 2009).

The compatibility limit of stearyl alcohol in a clear PVC compound is given as 2.6% (Nass & Heiberger, 1988). Probably, the low temperatures in the storage facility have caused the level of stearyl alcohol in the PVC compound to rise above its saturation concentration and lead to its exudation. In contrast to lubricants, plasticizers are accepted in PVC at a high concentration, and compatibility limits are in general not a matter of concern (Wilson, 1995).

It is interesting to note that rigid PVC does not show the same compatibility problems as flexible PVC. In the latter, the plasticizer causes a more open structure by reducing the glass transition temperature ( $T_g$ ). This increases permeability and thus the risk of exudation

of incompatible additives (Wilson, 1995; Wilkes *et al.*, 2005). Stearyl alcohol added to a flexible PVC compound is thus expected to exhibit a higher risk of exudation than in a rigid formulation for which it is intended.

### Cleaning

Additives used specifically to aid processing have usually no influence on end properties (Wilson, 1995). Thus, removing stearyl alcohol from the surface of DanDolls is not believed to have an impact on their long-term stability. Rather, the white bloom affects the appearance of the dolls to such a degree that removal is justified. However, removal of exuded plasticizers during cleaning is a subject of concern, since this can cause further leaching of plasticizer from the bulk, which may compromise the stability of the PVC object (Sale, 1988; Morales Muñoz *et al.*, 2014). However, removal of already exuded plasticizers cannot be avoided to obtain a clean surface, and is often accepted as long as further plasticizer is not extracted from the bulk (Morales Muñoz *et al.*, 2014).

Because of the risk of such extraction, the use of organic solvents are, in general, discouraged (when used undiluted) (Morales Muñoz *et al.*, 2014). However, some detergents have been recommended for use with demineralized water (Morales Muñoz, 2011; Balcar *et al.*, 2012; Morales Muñoz *et al.*, 2014). Dry cleaning might seem the safest method to avoid plasticizer extraction. However, dry cleaning is rarely effective (Morales Muñoz, 2011) and moreover risks scratching the plastic surface, whereas moisture acts as a lubricant which can reduce the risk of scratches (Balcar *et al.*, 2012). In particular, cotton swabs have been discouraged for dry use on plasticized PVC, because they have been found to cause severe changes to the topography of the surface (Morales Muñoz, 2010). Instead, PEL-Cloth™ is recommended as a safer and more effective method





**Figure 8** The Dandolls from Fig. 1 after treatment. The dolls look as if new, with no signs of degradation.

(Morales Muñoz, 2010). On the basis of these studies, PEL-Cloth<sup>TM</sup> moistened with demineralized water was used to clean DanDolls, an approach which removed the stearyl alcohol easily. Only in remote areas such as ears and nostrils, the dolls were cleaned with small moist cotton swabs. After cleaning, the dolls looked as if new, with no sign of degradation (Fig. 8; compare Fig. 1A and B).

## Conclusion

This study investigated the bloom of a white, waxy material, which was observed after 10 years of storage on more than 130 PVC dolls produced by Dan Hill Plast A/S in the 1980s and 1990s. By FTIR, the white bloom was identified as predominantly stearyl alcohol, which is not an additive generally used for flexible PVC. Stearyl alcohol is known to be used as a flow promoter in rigid PVC formulations, and it is proposed that it had been added to the flexible PVC compound with a similar purpose in mind. The bloom was independent of the plasticizer in the bulk PVC compound and was found on PVC dolls containing phthalate plasticizer as well as on dolls containing ATBC plasticizer.

The low temperature in the storage is believed to have played a decisive role in the formation of the bloom by causing a reduction of the compatibility of the stearyl alcohol in the PVC compound. This was confirmed by observing considerable reabsorption of stearyl alcohol into the surface of the dolls after a month at room temperature, as well as reappearance of stearyl alcohol after the dolls were brought back to cold storage. The observation indicates that the phenomenon is, to some degree, reversible. Dan Hill Plast compounded the plastic themselves, and it is likely that this phenomenon is restricted to items made with their formulation, and not a problem found in general on PVC dolls. Dan Hill Plast had a significant production and export of dolls, among other items, their production of precious collection

dolls, and acquirers should be aware of the phenomenon when considering storage.

It is likely that storing the dolls at room temperature would mitigate the bloom and thus the necessity of cleaning. However, the benefit of storage by higher temperatures should be weighed against the problems this is known to cause, such as increasing the rate of plasticizer loss. Whereas plasticizer loss is known to compromise the long-term stability of the PVC compound, the release of the stearyl alcohol is not believed to have the same impact on the long-term stability. Thus it cannot be recommended to store the dolls at higher temperatures. However, since the stearyl alcohol is apparently reabsorbed to some degree when returned to room temperature, it is recommended that the dolls are taken out of cold storage in good time (e.g. a month) before cleaning is planned. This will not only facilitate cleaning, but also minimize the removal of original material.

Other dolls, which had been donated to the Conservation Centre in Vejle due to their extreme bloom of white, crystalline material, were compared with the bloom on DanDolls. In this case, the bloom consisted of stearic acid, which is a common additive in flexible PVC to aid release of the compound from the moulds during processing.

In both cases, the white bloom is believed to happen because of inherent compatibility problems between the additive and the plastic matrix.

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## List of suppliers


References: cetyl alcohol (>99.5%), stearyl alcohol (>99.5%), ATBC, (>98%), DINP (>99%, mixture of isomers), stearic acid (97%), acetonitrile (>99%), and MTBE (99.9%) were all obtained from Sigma-Aldrich and used as received.

PEL-Cloth<sup>TM</sup> made from polyester/polyamide ultra micro fibres. Obtained from Preservation Equipment Ltd, England. <https://www.preservationequipment.com>.

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